



FABRICATION AND CHARACTERIZATION OF PASSIVE SAMPLER USING POLYMERIC INCLUSION MEMBRANE (PIM) AS DIFFUSION LAYER FOR PHOSPHATE MEASUREMENT

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ABSTRACT

The PIM-passive sampler is a passive sampler using PIM as a diffusion layer. This research aimed to optimize the concentration of PIM plasticizer and the concentration of phosphate ions in bulk solution to produce a PIM-passive sampler for phosphate measurement with high accuracy. In this study, a passive sampler was made of a 15 ml glass bottle containing 0.2 M H₂SO₄ solution as the receiving phase and PIM as a diffusion membrane. PIM was prepared by mixing polyvinyl chloride (PVC) as the base membrane, Aliquat 336-Cl as a carrier, and 1-decanol as a plasticizer. Sampling was done by immersing the passive sampler in the bulk phase solution for three hours. The phosphate concentrations in bulk and receiving phases were determined regularly every 30 minutes using the visible spectrophotometric method at a wavelength of 690 nm. The results showed that the optimum concentration of 1-decanol for PIM was 15% w/w. The higher the plasticiser concentration, the PIM was oily, thus preventing the analyte from contacting the extractant. The range of phosphate ion concentrations in the sample that the PIM-passive sampler could detect was 0.1-1.3 mg P/L. The calibration curve for phosphate measurement was $C_{TWA} = 1.0664 \cdot Cs - 0.0088$ with a correlation coefficient (R^2) was 0.9998. This shows that the PIM-passive sampler can be used for the measurement of phosphate ions with high accuracy.

Keywords: PIM, passive sampler, phosphate, 1-decanol, Aliquat 336-Cl.

INTRODUCTION

Phosphate is a key nutrient in the process of algae growth blooming that is known as eutrophication. Phosphate sources in aquatic systems are from natural and human activities, one of which is synthetic fertilizers in agricultural activities. Among phosphate species, dissolved reactive phosphates are phosphate species consumed directly by aquatic biota (phytoplankton) in their metabolism. For this

reason, it is necessary to monitor the concentration of phosphate in the aquatic environment in the context of water resources management. Eutrophication can emerge when the concentration of dissolved phosphate is more than 0.1 mg/l. For the management of aquatic environments, phosphate detection at a concentration lower than 0.1 mg/L is needed. However, low phosphate concentrations are often not detected by spectrophotometric analysis methods developed by Murphy and Riley.

[1]. Various methods were developed to preconcentrate phosphate from samples, for example, the coprecipitation method using Mg [2], HPLC [3], and SPE (Solid Phase Extraction) using zirconia as adsorbent [4]. These preconcentration methods were offline sample pretreatment technique that requires a large sample volume. Flow system based methods (online) called Flow injection analysis (FIA) have been developed for phosphate preconcentration using an anion exchange column [5] and using Polymeric Inclusion Membrane (PIM) [6]. The online preconcentration method is faster and more efficient than the offline method. However, in these methods, water sampling is carried out by grab sampling means that water samples are collected at one location and at one point in time, so we can not predict the time average concentration of phosphate in the aquatic environment.

The passive sampler was developed to overcome the obstacles, including time constraints, costs, Physico-chemical changes of analytes, and concentrations of analytes small enough to be directly measured. By using the passive sampler, the analyte from the bulk phase will be accumulated into the receiving phase in the sampler through the membrane phase as a diffusion layer for a certain period. The concentration of analyte detected by the passive sampler (formulated as time-weighted average concentration, C_{TWA}) results from the concentration of analyte accumulated in the passive sampler by considering the diffusion rate of the analyte through the diffusion layer.

The existing passive sampler for phosphate detection uses the Chemcatcher

with the Empore™ Anion SR extraction disk as the receiving phase [7]. After completion of sampling, the phosphate adsorbed on the disk was eluted using 0.5 M HCl. This procedure was able to elute up to 90% phosphate. DGT-based passive samplers have also been developed for in situ measurements of phosphates in water using various types of binding gels, including Cerium oxide [8] and zirconium oxide [9]. As with the chemcatcher, the phosphate accumulated in the DGT binding gel can be eluted with acid before measurement of its concentration. The selection of acid for elution determines the success of the chemcatcher and DGT passive sampler for phosphate measurement.

Other passive sampler devices have been explored for measurement chemicals in aquatic system. In this device, PIM was used as a diffusion layer. Passive samplers with PIM layer have been investigated to measure the concentration of ammonia [10], arsenate [11], and zinc [12]. Studies on the PIM-passive sampler for phosphate measurement have not been reported. However, transport and preconcentration phosphate combined with Flow Injection Analysis (FIA) has been reported [6]. In the research, PIM was prepared from PVC as base polymer and Aliquat-336 chloride as a carrier without plasticizer. Plasticizers can be added to the PIM to increase the membrane flexibility and softness, and the flux of targeted ion [13]. Therefore, in this following research, the PIM consisted of PVC, Aliquat 336 chloride, and 1-decanol as plasticizer was fabricated and used as a diffusive layer of the passive sampler for phosphate measurement. The

performance of passive sampler with PIM produced at various concentration was investigated in this study. The sampling rate (Rs) was calculated to determine the optimum concentration of plasticizer for PIM. In addition, the accuracy of phosphate measurement using PIM-passive sampler was also studied.

METHODS

1. Materials, Tools, and Instrumentations

Chemicals used for preparing PIM were high molecular weight Polyvinyl Chloride (PVC) (Merck), 1-decanol (Merck), Aliquat 336-Cl (Merck), and Tetrahydrofuran (THF) (Merck). Phosphate solution stock was prepared by dissolving KH_2PO_4 (Sigma) in demineralized water. H_2SO_4 (98%, Merck) was used to prepare the receiving phase. Ammonium molybdate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$) (Sigma) and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (Merck) were reagents for phosphate detection. Concentrations of phosphate in bulk and receiving phases were determined using the Shimadzu UV 1601 Spectrophotometer.

2. PIM Preparation

PIM was prepared by dissolving the amount of PVC base polymer in 10 ml of THF solvent. Afterwards, Aliquat 336-Cl and 1-decanol were added to obtain a total membrane weight of 300 mg. The carrier concentration was fixed at 30% w/w while the plasticizer concentration was varied from 5 to 25% w/w.

The membrane solution was then poured into a glass mold with a diameter of 6 cm and covered with filter paper and a watch glass to evaporate the solvent slowly. After

24 hours, a thin, flexible and transparent membrane was formed. The membrane is a cut circle with a diameter of 2.2 cm and functions as a diffusion layer for the passive sampler.

3. Passive sampler device

The passive sampler device consists of a glass bottle with a volume of 15 mL with two top and bottom openings with a diameter of 1.6 cm and 2.2 cm, respectively. The top opening is closed with a screw cap and is used to take the internal phase in the passive sampler bottle. The bottom opening is fitted with a screw cap with a hole with a diameter of 1.1 cm. PIM was cut in a circle with a diameter of 1.1 cm, clamped between the Teflon ring and rubber ring, and placed on the bottom opening. Parts of the passive sampler can be seen in [Figure 1](#).

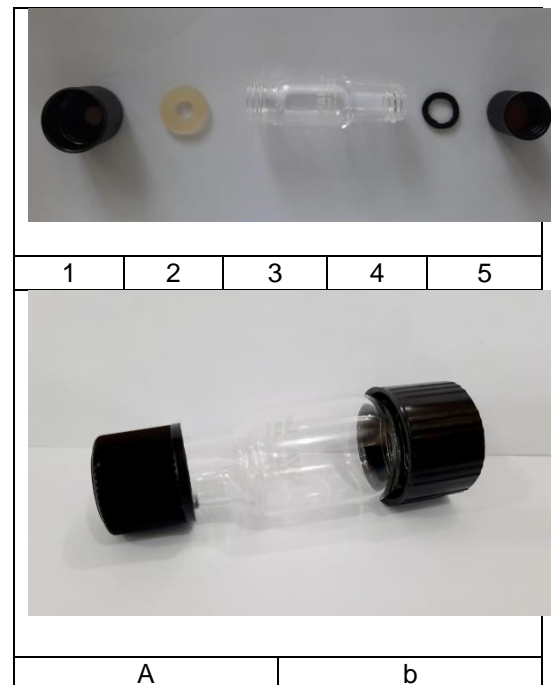


Figure 1. Parts of the passive sampler: (1) bottom cap, (2) Teflon ring, (3) passive sampler bottle, (4) rubber ring, (5) top cap; and ready-to-use passive sampler: (a) the top part, (b) the bottom part.

4. Passive Sampling Experiment

A passive sampling experiment was conducted in the laboratory. The parts of the passive sampler were assembled by incorporating Aliquat 336 chloride-decanol based PIM and 15 mL of 0.2 M H₂SO₄ as the receiving phase. The passive samplers were placed in a polypropylene test tube rack in a vertical position where the PIM side was facing down. The test tube rack and the passive samplers were positioned inside a container containing 10 L of 0.1-2.0 mg P / L phosphate solution as the bulk phase.

The aquarium pump was attached to one side of the container to imitate water flow as occurs in a natural aquatic environment.

Sampling was carried out for 3 hours. In every 30 minute, both the bulk and receiving phase were sampled for 4 mL and the phosphate concentration was determined.

Phosphate concentrations measured using a passive sampler (C_{TWA}) can be calculated using Eq. 1 below [14].

$$C_{TWA} = \frac{C_r \cdot V_r}{R_s \cdot t} \quad (1)$$

C_r is the phosphate concentration in the receiving phase (mg / L). V_r is the volume of the receiving phase (L). R_s is the sampling rate (L / min) obtained from the slope of the linear curve between the equivalent volume (V_{eq}) to the sampling time (t , minutes), as shown in Eq. 2.

$$V_{eq} = R_s \cdot t \quad (2)$$

$$V_{eq} = m_r / C_s, \quad (3)$$

V_{eq} can be calculated by Eq. 3, where m_r is the mass of the phosphate ion in the receiving phase (mg) and C_s is the

concentration of phosphate in the bulk phase or sample (mg / L).

5. Determination of phosphate concentration

The concentration of phosphate ion was determined using standard procedure as stated in Standard Methods [15]. For determination, 10 ml of sample was reacted with 0.4 ml of molybdate reagent and 0.05 ml of SnCl₂ reagent, then shaken well and waited for 10-12 minutes. The absorbance of the solution was determined using UV-Vis spectrophotometre at wavelength of 690 nm.

RESULTS AND DISCUSSION

1. Characteristics of PIM

PIM is the development of a liquid membrane after a bulk liquid membrane (BLM), an emulsion liquid membrane (ELM), and a supported liquid membrane (SLM). PIM has the same way of working as SLM, which is capable of simultaneous extraction and reverse extraction. Low carrier stability as an extractant in SLM [16], [17] can be overcome by using PIM because the release of the carrier can be prevented [13]. PIM is made by using a thermoplastic base polymer, for example, PVC. The polymer chains are straight, so there are no cross-links between the polymer chains, causing PVC to dissolve easily in solvents such as THF. The mechanical strength of PIM comes from the intermolecular forces and the entanglement between the chains [18].

Aliquat 336-chloride (trialkylmethylammonium chloride) is often used as a carrier for PIM. The three alkyl groups in Aliquat 336-Cl are mixtures of the C₈-C₁₀ chain [19]. PIM with a composition of 70% PVC and 30%

Aliquat 336-chloride (% w / w) has been used as a diffusion membrane in simultaneous phosphate measurements using flow analysis. [6]. The composition used in the study adopted PIM, which is used for the extraction of arsenate ions [20].

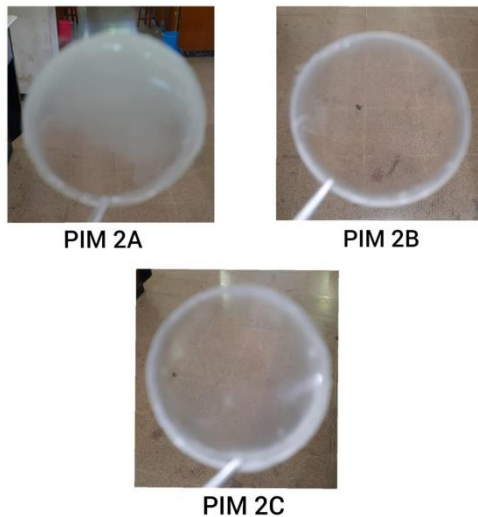


Figure 2. PIMs were prepared using PVC, Aliquat 336-Chloride, and 1-decanol at a composition of 55%:30%:15% (w/w) from three batches (A, B, dan C).

As shown in Figure 2, the PIM produced is physically transparent and thin. The presence of parts that appear cloudy on the PIM is due to differences in the humidity of the mold used from three batch at the same PIM composition. To prevent this, the mold must be completely dry before use. Passive sampler test, the transparent part of the membrane was cut in a circle with a diameter of 2.2 cm. By using a glass mold with a diameter of 6 cm, the resulting membrane has a thickness of $30 \pm 0.5 \mu\text{m}$. The resulting membrane did not undergo swelling during the sampling process (3 hours) where the weight of the membrane before and after sampling was relatively the same, namely 0.057 ± 0.009 grams.

2. Optimization of Plasticizer Concentration

The intermolecular forces contained in PIM are mainly Van der Waals forces which are weak and non-specific. On the other hand, the stronger polar-polar interactions only occur in polar functional groups, namely the C-Cl groups in PVC. This can cause the membrane to become stiff, inflexible and reduce the diffusion of analytes across the membrane [21].

A plasticizer is added to increase the flexibility of the membrane so that the analyte can diffuse better. The polar group of plasticizer interact with the polar groups in the membrane so that the membrane becomes flexible. In addition, plasticizer molecules increase the distance between polymer molecules, thereby reducing the strength of intermolecular forces [21]. The concentration of plasticizer in PIM affects the transport and accumulation of phosphate ions in the passive sampler, so that it affects the accuracy of the passive sampler as a device for the measurement of phosphate ions. To determine the membrane composition that produces good transport and measurement of phosphate ions, in this research, 1-decanol was used as a plasticizer at various concentrations even though the extractant Aliquat 336-Cl contains 2-5% (w/w) 1-decanol [19].

The effect of plasticiser concentration on the accumulation of phosphate ions in the passive sampler is shown in Table 1. It can be seen in Table 1 that PIM made of PVC/Aliquat 336-Chloride/1-decanol was able to accumulate phosphate in the receiving phase. The amount of accumulated phosphate increased with an increase in the 1-decanol concentration up to 20% (w/w).

When using 25% plasticiser, the amount of phosphate accumulates was less.

Based on phosphate concentration in the receiving phase, the volume equivalent (V_{eq}) can be calculated using Eq. 3, while using Eq. 4, the phosphate sampling rate (R_s) can be determined. Based on the sampling rates obtained (Table 2), the C_{TWA} of phosphate could be determined from Eq. 1. Based on Figure 3, it can be seen that PIM with a composition of 55:30:15 (% w/w) can be used as a diffusion layer of a passive sampler for phosphate measurement with high accuracy (98.8%).

The low concentration of plasticiser causes the membrane to become stiff and easily damaged. Using PVC as the base polymer, the theoretical minimum concentration of 1-decanol is 18% w / w. Gibbons and Kusy [22] indicates that membrane performance will improve when using a plasticiser near the theoretical minimum concentration. From the research results, 1-decanol with a concentration of 15% (w/w) is the optimum concentration for PIM to be used as a diffusive layer in a passive sampler for phosphate measurement.

Table 1. The measured concentration of phosphate in the receiving phase of a passive sampler with PIM diffusive layer at various concentration of 1-decanol as a plasticizer

Time (minutes) / Plasticizer concentration (%w/w)	Measured phosphate concentration in the receiving phase (C_r , mg/L)				
	5	10	15	20	25
0	0.000	0.000	0.000	0.000	0.000
30	0.286 ± 0.037	0.347 ± 0.123	0.434 ± 0.123	0.260 ± 0.123	0.347 ± 0.123
60	0.477 ± 0.061	0.607 ± 0.123	0.694 ± 0.123	0.694 ± 0.123	0.521 ± 0.123
90	0.733 ± 0.061	0.781 ± 0.123	0.954 ± 0.123	0.954 ± 0.123	0.868 ± 0.000
120	0.998 ± 0.061	1.215 ± 0.123	1.215 ± 0.123	1.215 ± 0.123	1.128 ± 0.123
150	1.258 ± 0.061	1.388 ± 0.123	1.388 ± 0.123	1.475 ± 0.123	1.301 ± 0.123
180	1.432 ± 0.061	1.562 ± 0.123	1.648 ± 0.123	1.648 ± 0.123	1.388 ± 0.123

Table 2. The sampling rate (R_s) of phosphate measured with PIM-passive sampler

PVC : Aliquat 336-Cl : 1-decanol (%w/w)	R_s (L/minutes)
65:30:5	0.00008
60:30:10	0.00008
55:30:15	0.00008
50:30:20	0.00010
45:30:25	0.00008

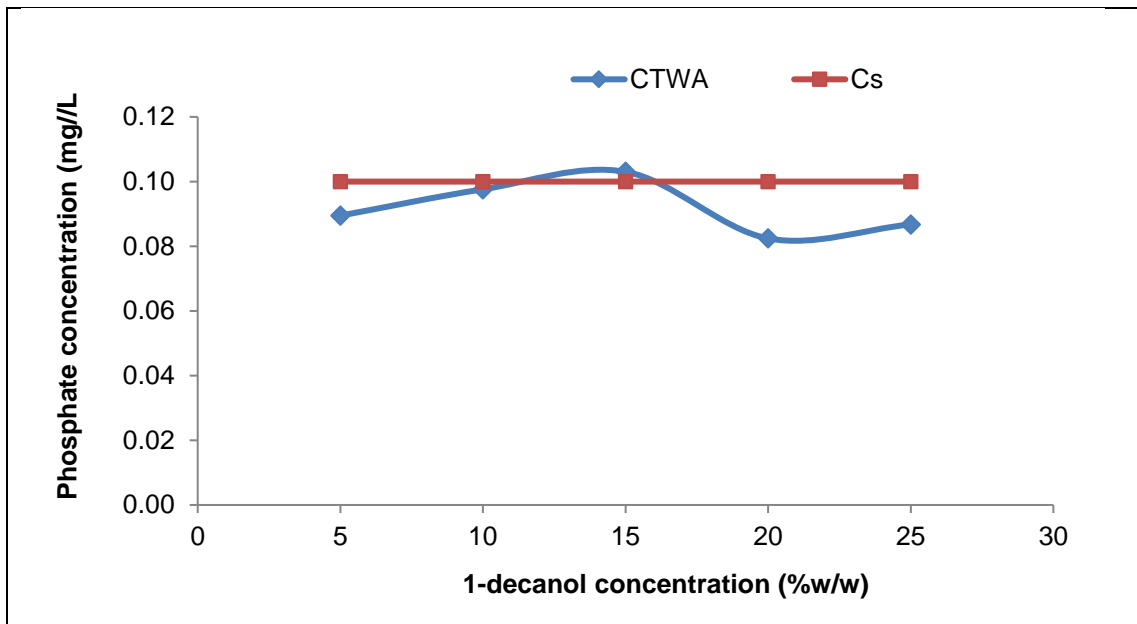
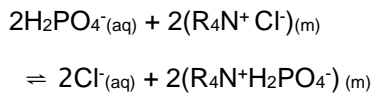


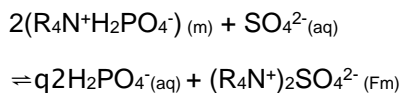
Figure 3. The effect of 1-decanol concentration on the C_{TWA} (blue) and C_s (red) of phosphate.

Transport of phosphate through PIM in the passive sampler is determined by the carrier used for the PIM. In this study, Aliquat 336-chloride ($R_4N^+Cl^-$) was used as a carrier. Aliquat 336-chloride (*n*-octylmethyl ammonium chloride, TOMAC) reacts as an anion-exchanger by forming an ion pair with anion from the aqueous phase. By using sulphate ion in the receiving phase, the phosphate transport could be proposed as below:

a. Bulk phase



b. Receiving phase



3. Calibration of Passive Sampler for Phosphate Measurement

Calibration of passive sampler is needed prior to the field sampling using a

passive sampler for determining the phosphate concentration at certain period of time. The passive sampler was used to measure phosphate at concentration range of 0.1-1.3 mg P/L. These concentration range of phosphate is primarily found in natural aquatic environments.

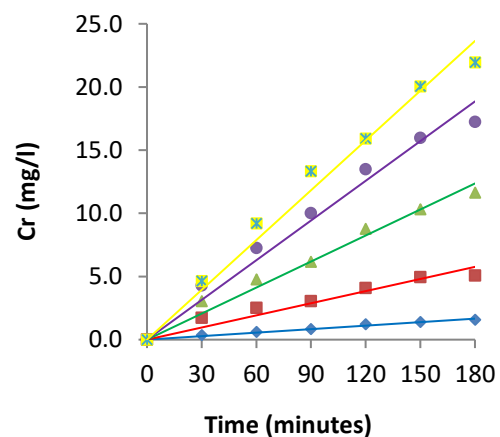


Figure 4. Phosphate concentration in the receiving phase of PIM-passive sampler for the following bulk phase concentrations: 0.1 (blue), 0.3 (red), 0.7 (green), 1.0 (purple), and 1.3 mg P/l (yellow). Passive sampler used PIM, which consisted of 15% w/w of 1-decanol.

Figure 4 shows linear diffusion of phosphate from the bulk phase to the receiving phase solution at five concentrations. It can be suggested that the gradient concentration of phosphate and sulphate between in bulk and receiving solutions causing the increase of the sampling rate of the phosphate at high concentration.

A linear calibration curve for phosphate measurement using a PIM-passive sampler was obtained at phosphate concentration in the bulk solution up to 1.3 mg/L, as shown in Figure 5 with the equation $C_{TWA} = 1.0664.C_s - 0.0088$ ($R^2 = 0.9998$) at 3 hours sampling period. Based on this equation, the concentration of phosphate in the field (C_s) during sampling period time can be calculated from the C_{TWA} .

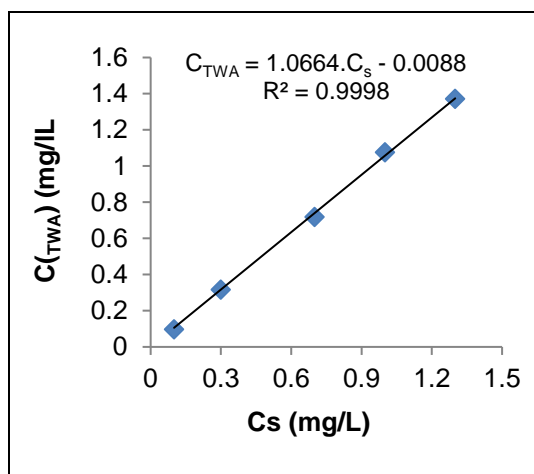


Figure 5. Calibration curve for phosphate measurement using PIM-passive sampler.

CONCLUSION

A PIM-based passive sampler could be used for phosphate measurement in an aquatic system. The optimum composition of PIM was 55% PVC, 30% Aliquat 336 chloride, and 15% 1-decanol (%w/w). PIM could be used as a diffusion layer in the

passive sampler device to measure phosphate concentration up to 1.3 mg/l with up to 99 % accuracy. For applications in natural aquatic environments, the presence of other anions in the sample may affect the detection of phosphate ions, so that it needs to be observed in further research.

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